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Polysilylated Unsaturated Molecules

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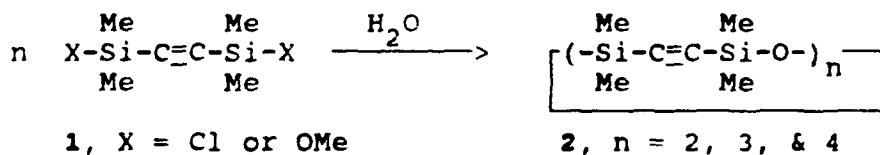
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Summary

A series of functionalized disilyl-substituted acetylenes, cyclic and linear polysilylpolyacetylenes and cyclic polysiloxypolyacetylenes were synthesized and characterized. The disilylacetylenes served as precursors to disilylated benzenes which were isomerized to their thermodynamically most stable meta isomers using molecular iodine as the catalyst. The studies on the oligomeric polysilylpolyacetylenes and the polysiloxypolyacetylenes included (1) the determination of their spectral and non-linear optical properties, (2) photochemical polymerization, (3) formation of complexes with transition metal carbonyls, and (4) studies of nucleophilic cleavage reactions aimed at determining suitable reagents and conditions for potential ring-opening polymerization reactions.

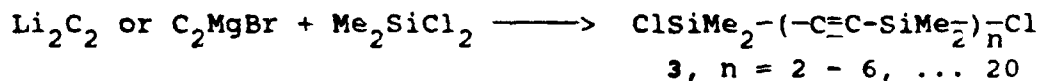
Summary of Results in Previous Reports

1. The high yield preparation and characterization of six novel bis(silyl)acetylenes, $X-Me_2Si-C\equiv C-SiMe_2X'$, **1**, with $X = X' = Me$, **1a**; $X = X' = H$, **1b**; $X = Cl$, $X' = H$, **1c**; $X = X' = Cl$, **1d**; $X = MeO$, $X' = H$, **1e**; and $X = X' = MeO$, **1f**.
2. The determination that the relative reactivity of **1** with *alpha*-pyrone to give *o*-bis(silylated)benzenes is $1f \approx 1d > 1e > 1c \gg 1a > 1b$, and that the arylsilanes formed from **1c-f** undergo an unusually facile hydrolysis or elimination to give a 1,3-disila-2-oxaindane derivative.
3. The discovery that molecular iodine is an effective catalyst for the isomerization of mixed disilylated benzenes to their meta isomers.
4. The finding that Vaska's complex, $Ir(CO)(Ph_3P)_2Cl$, is one of the few effective catalysts for direct conversion of alkynyl silanes to alkynyl-alkoxy silanes without cleavage of the acetylenic Si-C bond or concomitant hydrogenation of the triple bond.
5. The discovery of an unusual hydrolysis reaction of the bis(silyl)acetylenes, **1d-f**, which give high yields of the cyclic siloxy alkynes, **2**, $n = 2, 3$, and 4 ; with $n = 2$ predominating.



New Results

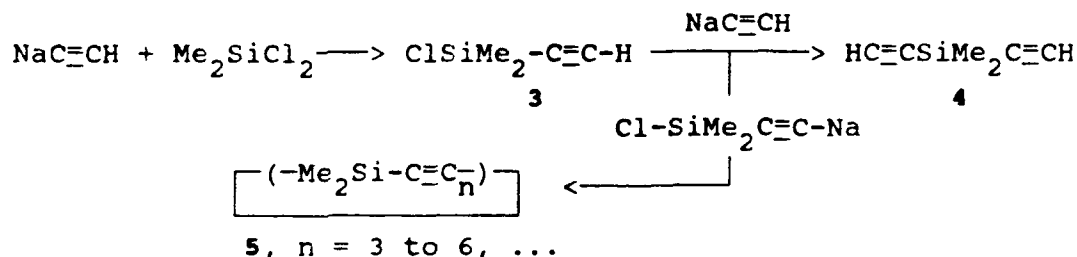
Syntheses: In the course of our preparation of the bis(silyl)acetylenes, **1**, we found that alkynyl substitution on silicon renders it more reactive towards nucleophilic reagents than ordinary chloro- or alkoxy- silanes. Thus, the reaction of dilithioacetylene or its Grignard analog with excess Me_2SiCl_2 in THF gives only low yields of **1d**. The major products from the reaction are oligomeric poly(silylacetylenes).



Significantly some of the oligomers obtained are highly colored, and give rise to bright burgundy red product mixtures. They are also remarkably viscous and high boiling for compounds of such low molecular weight. Oligomers with $n > 6$ are formed, but have yet to be separated or characterized due to our lack of the appropriate HPLC instrumentation.

For the $R = R' = \text{Me}$, $X = \text{Cl}$ system we have successfully applied this method to prepare oligomers with $n \geq 10$. The oligomers were capped with methyl or ethyl groups using the appropriate Grignard reagent. They were separated and characterized with respect to chain length by VPC ($n < 6$) and HPLC ($n > 6$) combined with mass spectral analysis. In addition their UV spectra ^1H , ^{12}C , and ^{29}Si NMR spectra were obtained and correlated.

Silyl substitution on the alkynes also enhances the acidity of the alkynyl protons relative to ordinary terminal acetylenes. Thus, in addition to the expected diethynyl dimethylsilane, **4**, the reaction of sodium acetylide with dimethyldichlorosilane gives significant yields of the cyclic silyl-alkynes, **5**, with $n = 5$ predominating. The cyclics presumably arise from a competing metallation reaction of the intermediate ethynyldimethylchlorosilane, **3**.

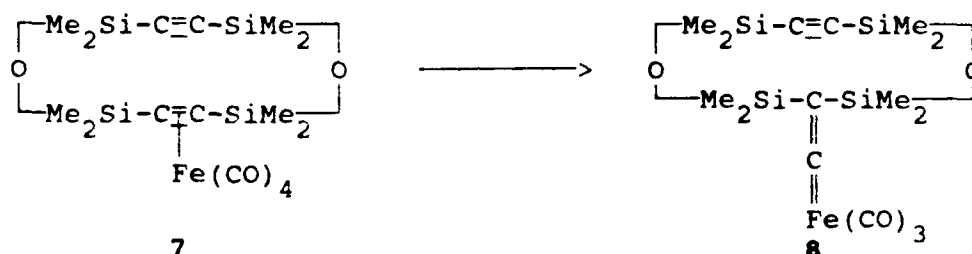


While one might expect the smaller rings, **5**, $n = 3$ or 4 , to be highly strained, unstable molecules, they are in fact quite stable crystalline solids with sharp, reproducible melting points. Very little is known about the chemistry of these polysilylpolyyne. It might well mimic the established chemistry of siloxanes and silicones. The hydrolysis of dimethyldichloro-silane and other difunctional organosilanes gives high yields of the cyclic siloxanes, D_3 , and D_4 , ($D = Me_2SiO$). The cyclic polyyne, **5**, $n = 3$ and 4 , are analogs of D_3 and D_4 in which electronegative oxygen with its two non-bonding electron pairs has been replaced with the electronegative $C \equiv C$ group having two pairs of π electrons. Similarly, **2**, $n = 2$, is an analog of D_4 with two of the oxygens replaced by acetylenes.

Chemical Properties: The polysilylpolyyne oligomers can be considered as analogs of siloxanes in which the oxygen with its two lone pairs of electrons has been replaced by the $C\equiv C$ linkage with its two π electron pairs. Polysilylpolyyne might thus combine the thermal stability of siloxanes with the chemical reactivity of alkynes. The photochemistry and acetylene metathesis chemistry of 2, $n = 2$, has been explored. This surprisingly stable molecule has a conformation which presumably holds the $C\equiv C$ linkages to the same plane and in relatively close proximity to each other. An intramolecular photochemical $[2 + 2]$ cycloaddition could give rise to

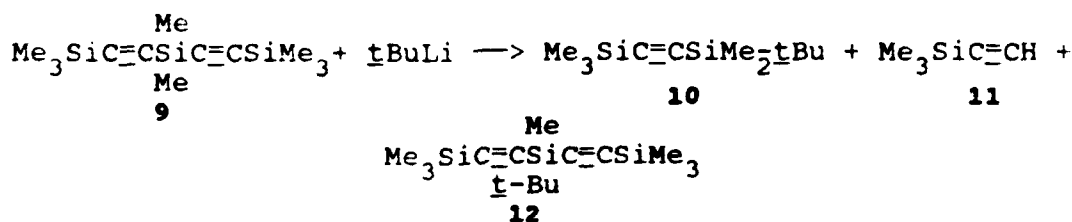
the cyclobutadiene derivative 6, constrained to the D_{2n} symmetry which is one of the forms of cyclobutadiene predicted by group theory to be stable. When 2, $n = 2$ is photolyzed in benzene solution an intermolecular polymerization occurs to give a material with an intriguing "step-like" macrostructure. We are in the process of trying to determine the molecular structure of this polymer which apparently arises from an intermolecular reaction of 2.

Reactions with Transition Metal Carbonyls: Compound 2, $n = 2$, also reacts with $Fe(CO)_5$ or $Fe_2(CO)_9$ to give a complex for which we originally suggested a ferrole structure.¹ We have since obtained an X-ray crystal structure of the complex which shows it to be the trimethylenemethane complex, 6, Figure 1. We believe that 6 may arise from an initially formed $\eta^2-Fe(CO)_4$ complex 7 by isomerization to the vinylidene iron complex, 8 which subsequently undergoes intramolecular cycloaddition to give the observed product, 6. In support of this suggestion, which assumes the intermediacy of the alkyne complex with $Fe(CO)_4$, we have found that 6 is not produced either thermally or photochemically in the reaction of 2 with the chalcone complex of $Fe(CO)_3$ which is known to be a convenient source of the $Fe(CO)_3$ fragment.² We also think that we have isolated the vinylidene complex 8 but it is not yet completely characterized.



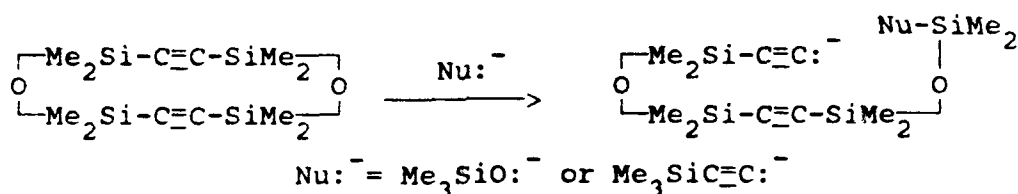
Compound 2, $n = 2$ also reacts with $Co_2(CO)_8$ to give the typical monoacetylene dicobalt complex, Figure 2, rather than the cyclobutadiene complex for which we had hoped. Reactions of 2, $n = 2$ with a variety of acetylene trimerization catalysts such as Volhardt's catalyst, $CpCo(CO)_2$,³ palladium on carbon in benzene,⁴ and the "soluble palladium" catalyst, $Pd(PhCN)_2Cl_2$,⁵ gave no evidence for polysilylated benzene formation.

Cleavage Reactions: In order to carry out possible equilibration and ring-opening polymerization reactions of both the linear and cyclic polysilylpolynes we initiated studies of nucleophilic cleavage reactions using bis(trimethylsilylethynyl)dimethylsilane, 9, and 2, $n = 2$ and model compounds. With alkoxide ions as the nucleophile 9 is completely degraded, giving D_n oligomers as the major isolated products after hydrolysis. However alkyllithium reagents react cleanly and rapidly at room temperature with 9 to give exclusively products arising from attack at the central silicon. With one equivalent of *tert*-butyllithium the main products are 10 and 11 after hydrolysis. An interesting minor product, formed in about 10% yield is compound 12 in which a substitution of a *tert*-butyl group for a methyl group has occurred at the central silicon. We have evidence that no free methylolithium is produced in the reaction and believe that 12 is formed by alkyl group exchange among pentacoordinate silicon intermediates.⁶



The cleavage reactions of 9 with lithium trimethylsilanolate, LiOSiMe_3 , have also been investigated. These produce rather interesting, apparently equilibrium, mixtures of silanolate and acetylide anions, presumably due to the similar basicity of the Me_3SiO^- and the $\text{Me}_3\text{SiC}\equiv\text{C}^-$ ions.⁶ We are in the process of completing the characterization of these mixtures and their derivatives with a variety of electrophiles.

We have also investigated the cleavage reactions of the cyclic siloxyalkyne, 2, $n = 2$. It undergoes complete degradation with alkylolithium reagents or with alkoxide ions. However either lithium trimethylsilanolate or lithium trimethylsilylacetylide, which are weaker bases, give clean initial cleavage of a silicon-carbon bond, indicating that these reagents are likely candidates for ring-opening polymerization reactions.



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6. K. D. Jo, unpublished results; "Cleavage Reactions of Silylacetylenes: The Case of the Missing Methyl Group," XXI Organosilicon Symposium, Montreal, Quebec, June 3-4 1988, Abstract No. P10.

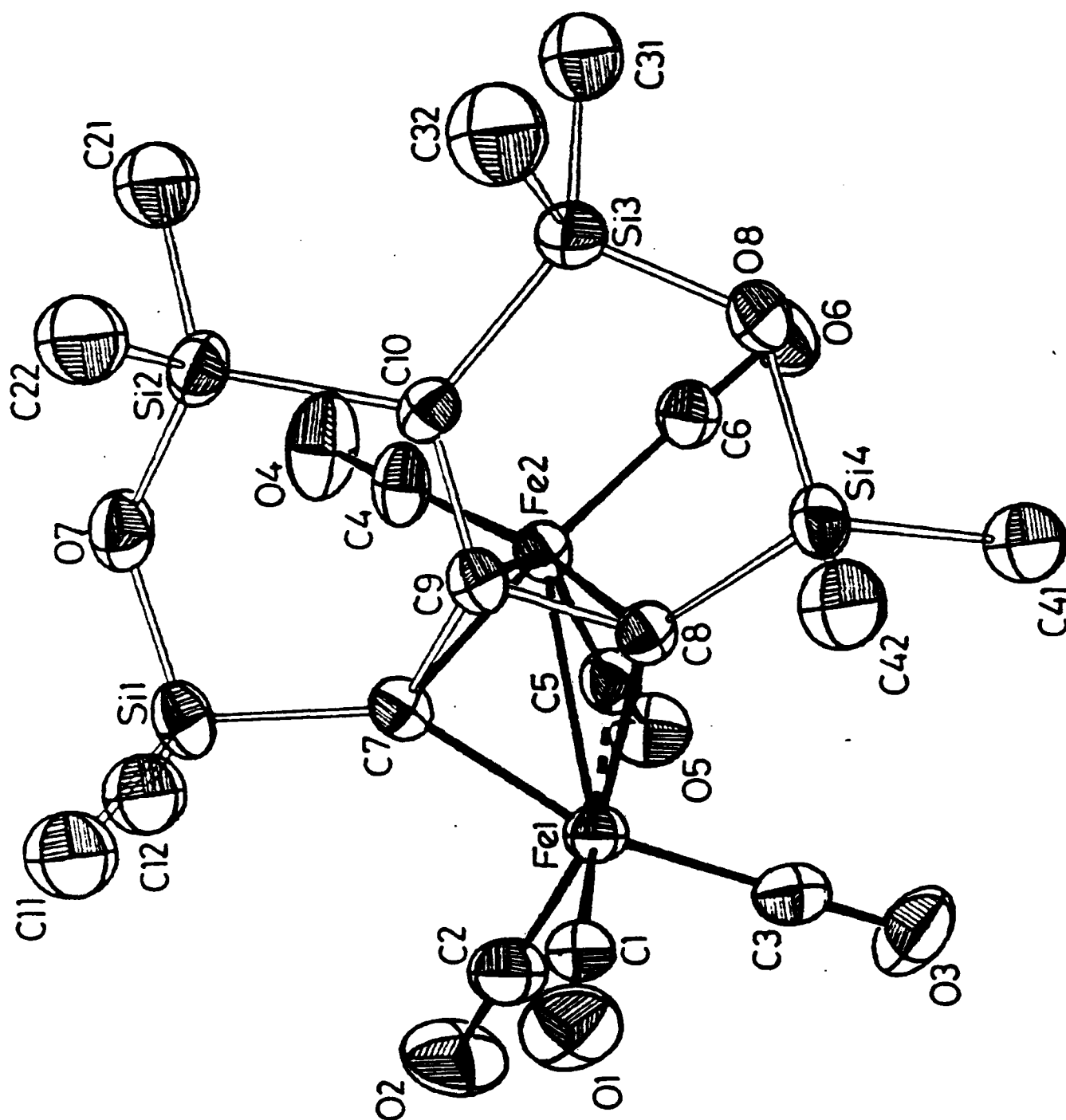


Figure 1. ORTEP drawing of the trimethylene-methane complex 6 formed by the reaction of 2, n = 2 with $\text{Fe}(\text{CO})_5$.

2

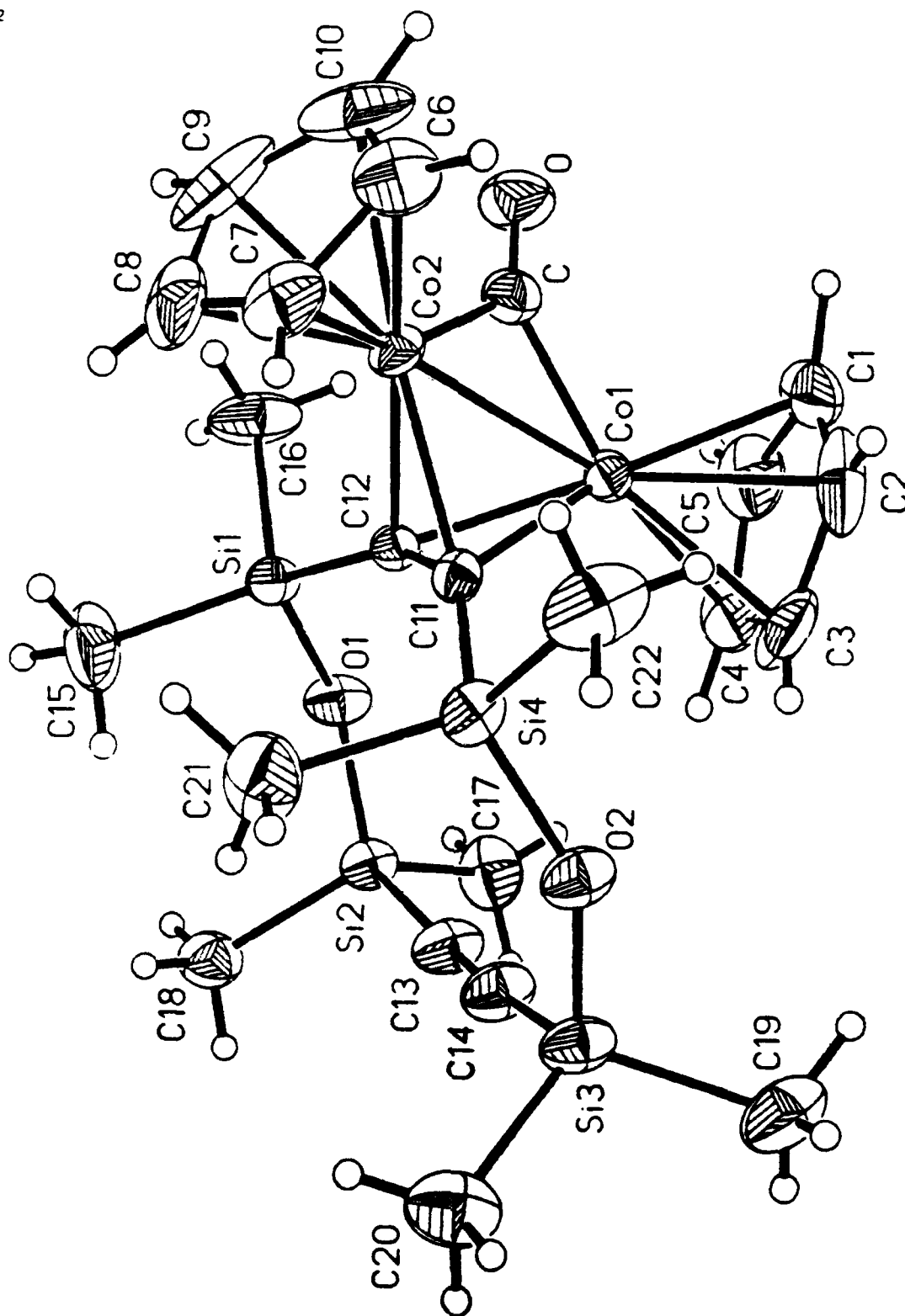


Figure 2. ORTEP drawing of the complex formed by the reaction of 2, n = 2 with $\text{Co}_2(\text{CO})_8$.

Cumulative Publications

"Silenes and Silenoids, 9. The Synthesis of Polyfunctional Bis(group 14)-substituted Cyclopentadienes via a Novel Cleavage Reaction of Silicon-Carbon Bonds by Chloride Ion," Rozell, J. M., Jr.; Jones, P. R.; Organometallics **1985**, 4, 2206-2210.

"The Synthesis and Reactivity of Polysilylacetylenes: Diels Alder Reactions to Give Bis(silyl)benzenes," Jones, P. R.; Albanesi, T. E.; Gillespie, R. D.; Jones, P. C.; Ng, S. W.; Appl. Organomet. Chem., **1987**, 1, 521-528.

"Polysilylpolyyne, 2. Intramolecular Dimerization of a Cyclic Siloxydiyne to Give a Novel Trimethylenemethane Complex," Jones, P. R.; Albanesi, T. E.; Cowley, A. H.; Nunn, C.; Organometallics, submitted.

Anticipated Papers:

"Polysilylated Unsaturated Molecules. An Unusual Iodine Promoted Isomerization of Aryl Silanes," Jones, P. R.; Jones, P. C.; Gillespie, R. D.; J. Organomet. Chem.

"The Catalytic Conversion of Bis(dimethylsilyl)acetylene to Bis(methoxydimethylsilyl)acetylene," Jones, P. R.; Albanesi, T. E.; Jones, P. C.; Gillespie, R. D.; Appl. Organomet. Chem.

"Polysilylpolyyne 3. Unusual Condensation Reactions of Bis(silyl)acetylenes: A Convenient Synthesis of Cyclic Siloxyalkynes," Jones, P. R.; Albanesi, T. E.; Smith, T. R.; J. Organomet. Chem.

"Polysilylpolyyne 4. Thermal and Chemical Redistribution Reactions of Diethynyl silanes," Jones, P. R.; Jones, P. C.; Ward, G. B.; Jo, K. D.; Organometallics.

Polysilylpolyyne 4. Reaction of Alkylolithium Reagents with Bis(trimethylsilylethynyl)dimethylsilane: An Unusual Methyl Substitution Reaction," Jones, P. R.; Jo, K. D.; Organometallics.

Polysilylpolyyne 5. Alkoxide Promoted Cleavage and Redistribution Reactions of Diethynylsilanes," Jones, P. R.; Jo, K. D.; J. Organomet. Chem. "Unusual Chemical and Physical Properties of Polysilylpolyyne," Eighth International Symposium on Organosilicon Chemistry, St. Louis, MO, USA, June 7-12, 1987, Paper No. A35.

"Thermochemistry of Polysilylpolyyne," 194th National Meeting of the American Chemical Society, New Orleans, LA, Aug. 30-Sept. 4, 1987, Abstract No. INOR 061.

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Graduate Students: James M. Rozell, Jr. Ph. D., Chemistry, Dec. 1985, Dissertation "The Chemistry of Polysilylcyclopentadienes."

Todd E. Albanesi, M. S., Chemistry, May 1987, Thesis: "The Synthesis and Reactivity of Bisisilylacetylenes."

Alan S. Goeringer, M. S., Natural Philosophy, May 1987

Kyo Dong Jo, anticipated Ph. D., 1989.

Shi-nien Uang, anticipated Ph. D., 1990.

Chung-jeng Lai.

Undergraduate Students: Ralph D. Gillespie, B. S. Chemistry (Rice), May, 1985.

Gary B. Ward, B. S. Physics, May 1987.

Todd R. Smith, B. S. Chemistry, Dec. 1987.

Charles W. Knight, anticipated B. S. Chemistry, 1991.

Interactions

Papers at Scientific Meetings

"The Synthesis of New Bis(dimethylsilyl)acetylenes and the Formation of Novel Cyclic Diyne and Triyne Siloxanes," 18th Meeting in Miniature of the ACS, Denton, TX, April 19, 1985, Abstr. No. 25, with T. E. Albanesi and R. D. Gillespie.

"Lithium Chloride Catalyzed Cleavage of Carbon Silicon Bonds in 1-(1-Trimethylsilylcyclopentadienyl)dimethylchlorosilane," 18th Annual Meeting in Miniature of the ACS, Denton, TX, April 19, 1985, Abstr. No. 48, with J. M. Rozell.

"Lithium Chloride Catalyzed Cleavage of Carbon Silicon Bonds in 1-(1-Trimethylsilylcyclopentadienyl)dimethylchlorosilane," XIX National Organosilicon Symposium, Baton Rouge, Louisiana, April 26-27, 1985.

"Metal Complexes of Bissilylcyclopentadienes." Southwest Organometallic Workshop, Norman, Oklahoma, May 31-June 2, 1985

"Polysilyllated Unsaturated Molecules. The Synthesis, Properties and Reactions of Functionalized Silylacetylenes," 190th National Meeting of the American Chemical Society, Chicago, Illinois, Sept. 8-13, 1985, Abstract No. INOR 31.

"Polysilyllated Unsaturated Molecules. An Unusual Iodine Promoted Isomerization of Aryl Silanes," 1985 Texas Mechanisms Conference, Round Top, TX, Oct. 11-13, 1985.

"Non-linear Optical Activity in Polysilylpolyacetylenes: Self Defocusing," 19th Meeting in Miniature of the ACS, Commerce, Tx, Apr. 25, 1986, Abstr. No. U10, with G. B. Ward, and T. E. Albanesi.

"The Catalytic Conversion of Bis(dimethylsilyl)acetylene to Bis(methoxydimethylsilyl)acetylene," 19th Meeting in Miniature of the ACS, Commerce, TX, April 25, 1986, Abstr. No. G3, with T. E. Albanesi, P. C. Jones, and R. D. Gillespie.

"Unusual Condensation Reactions of Bis(silylacetylenes)," 1986 Southwest Regional Meeting of the American Chemical Society, Houston, TX, Nov. 19-21, 1986.

"Unusual Chemical and Physical Properties of Polysilylpolyyenes," Eighth International Symposium on Organosilicon Chemistry, St. Louis, MO, USA, June 7-12, 1987, Paper No. A35.

"Thermochemistry of Polysilylpolyyenes," 194th National Meeting of the American Chemical Society, New Orleans, LA, Aug. 30-Sept. 4, 1987, Abstract No. INOR 061.

"Unusual Reactions of Iron Pentacarbonyl with a Cyclosiloxidyne: A Silyl-substituted Trimethylenemethane complex," 11th Annual Texas Mechanisms Conference, Round Top, TX, Oct. 9-11, 1987.

"Cleavage Reactions of Silylacetylenes," 21st Meeting In Miniature of the ACS, Arlington, TX, April 22, 1988, Abstr. No. G26, with K. D. Jo.

"Nucleophilic Cleavage Reactions of Silylacetylenes," J. J. Zuckerman Organometallic Chemistry Workshop, University of Oklahoma, May 27-29, 1988.

"Cleavage Reactions of Silylacetylenes: The Case of the Missing Methyl Group," XXI

*Organosilicon Symposium, Montreal, Quebec, June 3-4 1988.

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